

Optimal Control of Multiphoton Ionization Processes in Aligned I_2 Molecules with Time-Dependent Polarization Pulses

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Multiphoton ionization processes in *aligned* I_2 molecules are actively controlled by the homemade pulse shaping system, with which a time-dependent polarization pulse can be generated and controlled. We find a correlation between a femtosecond time-dependent polarization pulse and the production efficiency of evenly or oddly charged molecular ions. We achieve much better controllability of the correlation with a time-dependent polarization pulse than with a pulse having a fixed ellipticity. The results suggest the existence of an unknown tunnel ionization mechanism which is characteristic of a time-dependent polarization pulse. Our experiments point to new directions in optimal control studies with molecular systems, as discussed in the text.

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Based on the combination of the femtosecond pulse shaping technique [1] associated with the state-of-the-art ultrafast laser technologies and optimization algorithm, it has become possible to optimize quantum processes in atoms and molecules and achieve the desired results with a learning-loop pulse shaping system [2]. This approach is versatile and applicable even to the laser-molecule system for which the accurate Hamiltonian is not known. It corresponds to the experimental solution of a time-dependent Schrödinger equation by the use of measured values and the subsequent feedback with an optimization algorithm. The meanings of such a class of study are summarized as follows: (1) to elucidate the interaction between an ultrafast laser field and a molecule by analyzing the optimized pulse, (2) to verify hypotheses, (3) to search new phenomena by optimizing a specific experimental parameter, and (4) to optimize experimental conditions. These meanings are complementary with one another.

Since its first proposal of feedback quantum control [2], many demonstrative experiments have been performed for molecular systems (Refs. [3–5], and references therein). However, in experiments performed in gas-phase molecules, they are randomly oriented and give only the averaged results concerning the molecular orientation. This limits the outcome of optimal control experiments and prevents us from studying the correlation between the laser polarization and the molecular axis. In fact, there are many important polarization dependent processes such as parallel (perpendicular) transitions and enhanced ionization [6–8]. Here we demonstrate optimal control experiment where a sample of *aligned* molecules [9,10] is employed for the first time to our knowledge. Another important feature of the present experiment is that a time-dependent polarization pulse [11,12] is used as a new control parameter. Better controllability obtained with a time-dependent polarization pulse than with a pulse having a fixed ellipticity suggests

the existence of an unknown underlying physics and can trigger theoretical investigations to elucidate it. Actually, this is the case of the present study. A time-dependent polarization pulse should be a powerful tool especially for a sample of aligned molecules. A special emphasis is placed on the fact that the present experiment is also the first demonstration where both external (rotation) and internal (ionization and excitation dynamics) degrees of freedom in molecules are simultaneously controlled. Our experiment should point to new directions in feedback quantum control and molecular physics experiments as discussed below.

Here we pay close attention to the multiphoton ionization processes in I_2 molecules. They have been theoretically and experimentally studied over decades. The molecule can ionize sequentially [13] or nonsequentially [14–16]. The nonsequential double ionization is caused by recollision: (1) First an electron tunnels through the potential modified by the strong linearly polarized laser field, (2) then the electron is driven by the field and returns to the parent ion after the field reverses its direction, and, finally, (3) in the electron-ion recollision that might follow, one of the remaining electrons is collisionally ionized if the recollision electron has a sufficient kinetic energy. If the polarization deviates very much from linear, when the electron returns to the ion, it is offset in the lateral direction and it can miss. As a corollary of nonsequential double ionization, we can expect that it contributes more to the production of evenly charged molecular ions such as I_2^{2+} than to that of oddly charged molecular ions such as I_2^+ and I_2^{3+} . It means that we can expect a correlation between the polarization of the laser field and the production efficiency of evenly or oddly charged molecular ions.

We experimentally investigate the correlation. Here an outline of the experimental setup (Fig. 1) is described and a fuller description can be found in our recent papers [17,18]. A pulsed supersonic beam of I_2 molecules is

introduced into a time-of-flight (TOF) mass spectrometer by expanding I_2 molecules (~ 1 Torr) buffered with argon gas (760 Torr) through a 0.25-mm-diameter nozzle. The molecular beam is parallel to the TOF axis and crossed at 90° by the focused laser beams. In order to align molecules, we use pulses from an injection-seeded Nd:YAG (Nd-doped yttrium aluminum garnet) laser (Quanta-Ray, GCR-130, wavelength $\lambda = 1064$ nm, pulse width $\tau \sim 12$ ns, and the peak intensity $I \sim 2 \times 10^{12}$ W/cm 2). The polarization direction is set to be parallel to the TOF axis and thereby the I_2 molecules are aligned along the TOF axis. Under the present conditions, the ensemble average of the squared alignment cosine is estimated to be ~ 0.7 by the two-dimensional ion imaging technique [9,10]. Intense femtosecond Ti:sapphire laser pulses (Spectra-Physics, Super Spitfire, central wavelength $\lambda \sim 800$ nm, $\tau \sim 45$ fs, and $I \sim 2 \times 10^{14}$ W/cm 2) are used to ionize the I_2 molecules. We carefully adjust the focal spot size of the femtosecond pulse to be smaller than that of the YAG pulse to ensure that we probe only aligned molecules that have been exposed to the YAG pulse. The fragment ions produced from photodissociation and Coulomb explosion are accelerated by a static electric field toward a micro-channel plate (MCP, Galileo, AP TOF-18) detector positioned on axis with the TOF axis.

We adopt a fitness function F defined by $F = I(1, 1)/[I(1, 0) + I(1, 2) + I(2, 1)]$, where $I(m, n)$ stands for the integrated I^{m+} signals of the fragmentation channel $I^{m+} + I^{n+}$ produced from $I_2^{(m+n)+}$. In general, higher laser intensities are needed to produce more highly charged molecular ions. In order to reduce such an intensity-dependent effect on the fitness F , we compare ion signals from both I_2^+ and I_2^{3+} (oddly charged molecular ions) with those from I_2^{2+} (evenly charged molecular ions). With a sample of aligned molecules, two fragmentation channels $(1, 1)$ and $(2, 0)$ produced from I_2^{2+} should be treated separately as discussed below.

The peak intensity of 2×10^{14} W/cm 2 (linear polarization) gives the ponderomotive energy of $U_p = 12$ eV. Depending on the phase of birth of the electron, it can recollide with its parent ion with the maximum kinetic energy of $3.17U_p = 38$ eV [14,15], which is enough to knock the remaining electron from I_2^+ (ionization potential ~ 20 eV) to produce I_2^{3+} by nonsequential double ionization caused by recollision. Using such femtosecond pulses, we measure the ellipticity dependence of the fitness F with the combination of a quarter-wave plate and a half-wave plate. The major axis of the elliptical polarization is kept parallel to the TOF axis, i.e., the molecular axis of aligned I_2 molecules. (See Fig. 1 and the orientation angle $\theta = 0$ in the present case. The orientation angle θ is defined by the angle between the major axis and the TOF axis.) This is the basis of including $(1, 1)$ and excluding $(2, 0)$ in the fitness F as the fragmentation channel from I_2^{2+} . We are interested in the contribution of the nonsequential double ionization to the production of I_2^{3+} , and the $(1, 1)$ channel is expected to be dominant

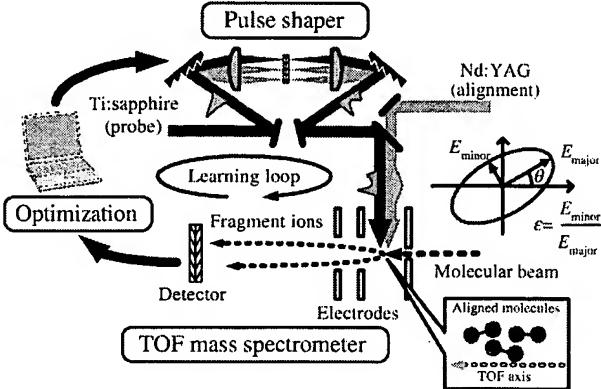


FIG. 1 (color online). An experimental setup. A pulse shaper is used to generate tailored femtosecond pulses for learning-loop optimal quantum control. Experimental feedback signals are collected from time-of-flight (TOF) mass spectra that result from the interaction of the tailored femtosecond pulses with aligned molecules. These signals are processed in a computer to iteratively improve the applied pulse shape based on genetic algorithm until an optimal result is obtained. Ellipticity ϵ and the orientation angle θ are also illustrated.

when the laser polarization is parallel to the molecular axis. This might be explained by the following simple consideration. An electron initially localized in one of the I atoms tunnels through the lower and thinner potential in between the two I atoms. The electron is driven by the laser field and returns to and recollides with the parent ion after the laser field changes its direction. Then the electron localized in another I atom should be more likely to be ionized because the slope of the molecular potential combined with the laser field is also reversed. In this case, the resultant fragmentation channel should be $(1, 1)$. On the other hand, when the laser polarization is perpendicular to the molecular axis, the ionized electron should be more likely to recollide with the I atom from which the electron was ionized. In this case the resultant fragmentation channel should be $(2, 0)$ [19].

The ellipticity ϵ is defined by the ratio of the minor axis to the major axis of an elliptical polarization and varies from $\epsilon = 0$ (linear polarization) to $\epsilon = 1$ (circular polarization). We accumulate ion signals with 2000 laser shots for each ellipticity and the results are presented in Fig. 2. The fitness F is 0.215 for linear polarization and gradually decreases down to 0.195 for circular polarization. It means that the relative production efficiency of evenly charged molecular ions (I_2^{2+}) is high for linear polarization and that of oddly charged molecular ions (I_2^+ and I_2^{3+}) is high for circular polarization, which is qualitatively consistent with our hypothesis. The contrast defined by (the maximum fitness)/(the minimum fitness) is ~ 1.1 . When we employ the $(2, 0)$ channel instead of $(1, 1)$ in the fitness F it presents opposite ellipticity dependence and increases as the ellipticity ϵ is increased. This observation can be explained by considering that the time period during which the electric field vector of the pulse

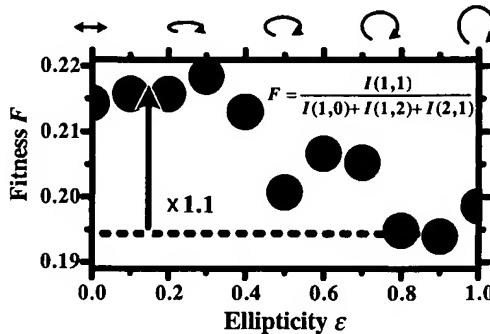


FIG. 2. Ellipticity dependence of the fitness F defined in the text. The contrast defined by (the maximum F)/(the minimum F) is ~ 1.1 .

is perpendicular to the molecular axis contributes to the production of the (2, 0) channel. These observations already demonstrate the efficacy of a sample of aligned molecules. When we include both the (1, 1) channel and the (2, 0) in the fitness F , we cannot observe any clear ellipticity dependence. This may be due to the mutual compensation of two different situations discussed in the previous paragraph, which can be validated by all these observations.

Then we optimize the fitness F with the homemade learning-loop optimal control system where a time-dependent polarization pulse can be generated and controlled [11,12]. We use a typical 4f configuration pulse shaper but remove polarizers to generate a time-dependent polarization pulse. We employ the genetic algorithm (GA) [20] as an optimization algorithm and search for an optimal time-dependent polarization pulse. We use the ellipticity for each frequency component as the only parameter in GA, and the phase for each frequency component is kept constant. As an initial pulse used in GA, we use a “randomly polarized pulse” for which the ellipticity for each frequency component is randomly defined. With a sample of aligned molecules, fragmentation signals in the TOF spectrum become sharper compared to those with randomly oriented molecules. Sharper and isolated signals are very advantageous to be used in the fitness F for feedback learning loop.

We maximize and minimize the fitness F and its evolutions are shown in Fig. 3 as a function of generation of GA. The maximum (minimum) fitness obtained is 0.34 (0.14) and the contrast is ~ 2.5 , which is much larger than that obtained with a fixed ellipticity (1.1). Our results show a much better ability to control the charged state of molecular ions with time-dependent polarization pulses than with elliptically polarized pulses having a fixed ellipticity. We characterize the optimal pulses with the technique known as POLLWOG (polarization labeled by interference versus wavelength of only a glint) [21]. The results are shown in Fig. 4. The intensity profiles of the optimized pulses are confirmed to be almost identical with those used in Fig. 2. The polarization is pre-

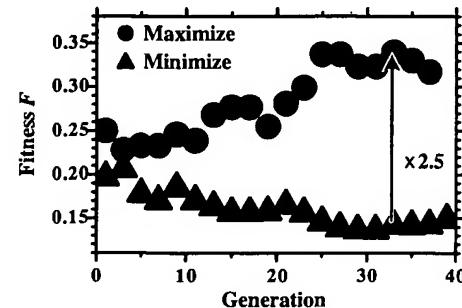


FIG. 3. The fitness F defined in the text is maximized and minimized as a function of generation of the genetic algorithm. The contrast defined by (the maximum F)/(the minimum F) is ~ 2.5 , which is much larger than that obtained with a fixed ellipticity as shown in Fig. 2.

scribed by both the ellipticity ϵ and by the orientation angle θ . When the fitness F is maximized, i.e., the production efficiency of I_2^{2+} is optimized with that of oddly charged molecular ions suppressed, the pulse becomes linear polarization parallel to the TOF axis ($\theta = 0$) at around the peak of the pulse. Such a polarization corresponds to the one which we consider to be a favorable situation for the production of the (1, 1) channel due to recollision. The peak intensity of $1.3 \times 10^{14} \text{ W/cm}^2$ gives the maximum recollision energy of $3.17 U_p = 24 \text{ eV}$, which is enough to knock the remaining electron from I_2^+ to produce I_2^{2+} by nonsequential double ionization caused by recollision. On the other hand, when the fitness F is minimized, i.e., the production efficiency of

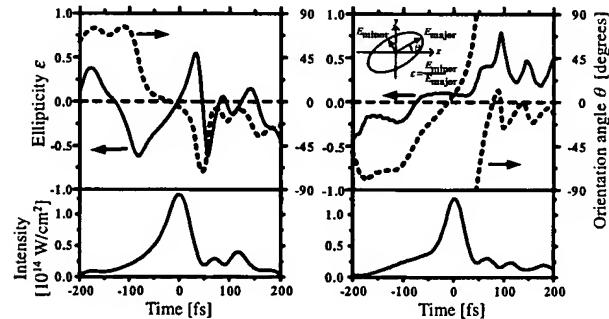


FIG. 4. The time-dependent polarizations and the intensity profiles of the optimized pulses characterized by the homemade POLLWOG system. In the upper panels, both ellipticity ϵ (solid curve, left ordinate) and the orientation angle θ (dashed curve, right ordinate) are presented. Ellipticity ϵ and the orientation angle θ are illustrated in the inset. The sign of ϵ is related to the helicity of the elliptical polarization. If positive values of ϵ define left elliptical polarization, negative values of ϵ define right elliptical polarization and vice versa. The lower panels show the instantaneous intensity profiles expressed as $I(t) = I_0 f(t)$, where I_0 and $f(t)$ are the peak intensity and the pulse time profile, respectively. The left and right panels correspond to the optimized pulses which give the maximum and the minimum F , respectively.

oddly charged molecular ions is optimized with that of I_2^{2+} suppressed, the ellipticity stays small ($\epsilon \sim 0.1$) from -60 to $+30$ fs, i.e., over the main part of the pulse. Here we note that the orientation angle changes more rapidly than in the maximized case and it goes through zero just as the case with the fitness F maximized. Qualitative features of the optimized polarizations are consistent with our expectations and the results shown in Fig. 2. In fact, the polarization becomes linear (elliptical) at around the peak (over the main part) of the pulse optimized to maximize (minimize) the fitness F . However, the ellipticity of ~ 0.1 over the main part of the pulse optimized to minimize the fitness F is rather small compared to the results shown in Fig. 2. The results suggest the importance of the time evolution of the potential energy surface associated with the increase of the internuclear distance as well as the electrons' dynamics discussed above.

Apparently, further theoretical studies are required to understand the underlying physics in the optimal control of the charged state of molecular ions. A tentative scenario is as follows: We note that the optimized pulses have polarization components perpendicular to the aligned molecular axis before (and after) the peaks in both cases of maximization and minimization of the fitness F . The polarization components perpendicular to the aligned molecular axis are preferable to a perpendicular transition such as $A^3\Pi_{1u} \leftarrow X^1\Sigma_g^+$ [22]. When the molecule is excited on a dissociative potential such as A state and the internuclear distance increases to the critical region of enhanced ionization, the molecule is in a favorable situation both for sequential and for nonsequential double ionization. In such a situation, there might exist a new ionization mechanism by which the ionization is enhanced even with a relatively small ellipticity. The generalization of enhanced ionization with a time-dependent polarization pulse, where electron localization, time evolution of internuclear distance, destructive interference between different excitation paths and/or molecular orbitals, and Landau-Zener transition should play important roles, is now in progress in our group and will be presented elsewhere in the near future [23].

In conclusion, we find a correlation between a femtosecond time-dependent polarization pulse and the production efficiency of evenly or oddly charged molecular ions using a sample of aligned molecules. Much better controllability of the correlation is achieved with a time-dependent polarization pulse than with a pulse having a fixed ellipticity. The novelty of our study is multifold and points to the following new directions in optimal control studies with molecular systems: (1) A sample of aligned molecules is used in the optimal control experiment for the first time. The use of aligned molecules enables us to find a correlation between the polarization of the laser field and the production efficiency of evenly or oddly

charged molecular ions, which should have been washed out with randomly oriented molecules. (2) In order to optimize the quantum processes in molecules, the time-dependent polarization pulse is applied to the learning-loop optimal control system for the first time. It does give a better controllability of the charged state of molecular ions than a pulse with a fixed ellipticity. The importance of the time-dependent polarization pulse is also pointed out to selectively prepare one of the enantiomers from the 50:50 racemates [24]. (3) Using a sample of aligned molecules and a time-dependent polarization pulse, both external and internal degrees of freedom in molecules are simultaneously controlled.

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